# Progress on Investigations of Confectionery Fats

Report No. 4
to
National Confectioners' Association
for
June 1, 1958 - June 1, 1959

By

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UNITED STATES DEPARTMENT OF AGRICULTURE
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NEW ORLEANS, LOUISIANA

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## FOREWORD

The research work on confectionery fats as described in this report was undertaken on considering the suggestions and recommendations of the Research and Development Committee of the National Confectioners' Association. The research work, particularly that performed by the Fellow of the National Confectioners' Association, is believed to conform with the wishes of the Committee. It was their recommendation that the priorities of the projects to be worked on should be: (1) completion of the evaluation of the cocoa butter like-fat already developed; (2) continuation of the studies of moisture transmission through fat-containing coatings, and (3) further exploration of the design of equipment for the evaluation of "temper" in both liquid and solid chocolate and also in confectioners' coatings. The objective of the research on cocoa butter-like fat was stated to be the development of a domestic fat which blends satisfactorily with cocoa butter, retards or prevents fat bloom, and is acceptable for use in warm climates.

The present report describes work performed by Dr. Werner Landmann, the Fellow of the National Confectioners' Association, as well as work performed by a number of individuals in the Industrial Crops Laboratory and the Engineering and Development Laboratory.

Report approved by:

Mr. T. H. Hopper, Chief
Industrial Crops Laboratory

## SUMMARY

A 140-pound sample of cocoa butter-like fat was obtained by combining the products obtained from 4 pilot plant runs. The products obtained from each of the 4 runs were practically identical, indicating that the process used was reproducible. The composite sample, called Sample No. 1, had a slight flavor and odor which could have been removed if this had been deemed necessary. The sample also contained about 20% of trisaturated and other high-melting triglycerides, which it was believed might improve the performance of the fat at summer temperatures.

Evaluation of Sample No. 1 by members of the Research and Development Committee revealed that in candy formulations the fat was responsible for difficulties in tempering and demolding. Eating quality was below expectation. There faults were believed to have been caused by the content of high-melting triglycerides.

Subsequently, a portion of Sample No. 1 was modified by removing the 20% of fat melting above 98.6° F. Tests with this modified fat revealed that it was better than Sample No. 1 but still was not satisfactory.

Using the data obtained with the above-mentioned samples and additional data developed in the laboratory, the method of preparing the cocoa butter-like fat was changed and a second sample was prepared in the pilot plant. This second product, Sample No. 2, was sent to members of the Research and Development Committee for testing. The tests should be completed in the near future.

While it cannot be claimed at this time that a satisfactory cocoa butter-like fat has been developed, definite progress is being made.

Research work on confectionery fats also was carried out in other areas. The investigation of the properties of the components of confectionery fats has revealed that 2-oleopalmitostearin, which comprises about 57% of cocoa butter, can solidify in four different forms; their melting points are 99.3, 91.4, 76.1, and 64.8° F. It also was found that 2-oleodistearin, which comprises about 22% of cocoa butter, solidifies in four forms, their melting points being 109.0, 99.9, 86.0, and 73.0° F. Expansivities and melting dilations of several of the forms were determined.

One phase of the investigation of the transmission of moisture through confectionery fats has been completed. Useful information was obtained, and two manuscripts describing the work have been prepared. Additional research on the transmission of moisture through fats is now underway.

An investigation of the effect of composition and polymorphic form on the hardness of fats was made. It was found that crystal size and the amount of tempering which a fat receives greatly affects its hardness. The addition of a normally liquid oil to a hard fat greatly decreases the hardness.

Several samples of a new type fat (essentially a mixture of dibutyrostearins and dibutyropalmitins) were prepared and submitted for testing as slab oils in the manufacture of candies. These tests have not yet been completed.

# REPORT

## A. Cocoa Butter-Like Fat

Objective. Approximately a year ago the Research and Development Committee of the National Confectioners' Association suggested that the research work on confectionery fats be redirected so as to give highest priority to the development of a cocoa butter-like fat. Prior to this time the emphasis in the research had been on the development of information on the properties of confectionery fats and their components so that the best possible performance might be obtained from existing fats. The purpose of the work on cocoa butter-like fats is to develop a product, derived from domestic oils, which will resemble cocoa butter and will be compatible with it.

Needless to say, if an acceptable cocoa butter-like fat should be developed, it would not displace cocoa butter; rather it would alleviate a situation of short supply and high prices.

A process for making a good cocoa butter-like fat should also be suitable for making other special confectionery fats. The greater availability of such fats should promote the production of nonchocolate types of fat-containing confections.

Method. Cocoa butter contains the same building blocks (essentially glycerol and oleic, stearic, and palmitic acids) found in abundance in domestic oils or easily derived from them. The problem is to recombine these building blocks both in the right proportions and in the right combinations within the individual molecules. Work in this area was performed at the Southern Regional Research Laboratory several years ago.

An article describing the process and products obtained has been published (R. O. Feuge, N. V. Lovegren, and H. B. Cosler, Journal American Oil Chemists' Society, vol. 35, p. 194-199 (1958)). Essentially the process consists of rearranging a mixture of a completely hydrogenated oil and an olein-rich oil. The rearrangement can be carried out in the same manner that lard is rearranged on a commercial scale. The second step of the process consists of separating the monounsaturated triglycerides (cocoa butter-like fraction) from the reaction product. This is accomplished by dissolving the reaction product in a suitable solvent, lowering the temperature, and collecting over the proper temperature interval the solid material which separates out of solution. This second operation also is practiced commercially.

While the above-described process will never produce a fat identical with cocoa butter in all respects, it has produced on a laboratory scale products which closely resemble cocoa butter. The process and products obtained from it are currently being evaluated on a pilot plant scale.

Preparation of Samples and Their Evaluation. The two fats used in the first pilot plant preparation were an almost completely hydrogenated cottonseed oil obtained from Anderson, Clayton & Company, Dallas, Texas[1] and a triolein product obtained from the E. F. Drew Company, Boonton, New Jersey[1].

The two fats, mixed in the ratio of 70 pounds of hydrogenated cottonseed oil to 30 pounds of triolein product, were subjected to the

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1/ It is not the policy of the Department to recommend or endorse the product of one company over similar products made by others. The name of the company is given merely as a matter of information.

rearrangement reaction. Briefly, the fat mixture was placed under a dry, inert atmosphere, a small amount of catalyst (sodium ethoxide) was added, and the mixture was stirred for 40 minutes at 156° F. The reaction product was washed with a dilute solution of acetic acid and with water to remove the catalyst.

The catalyst-free reaction product was dissolved in acetone, an inert solvent, in the weight ratio of 4 parts acetone to 1 part product. On cooling this solution to room temperature, 82° F., approximately 34% of high-melting fat solidified and separated out of solution. After this solid fat was removed, the solution was cooled to 29° F. Between these temperatures the cocoa butter-like fraction, consisting mostly of monounsaturated triglycerides, solidified and separated from the solution. The yield of this cocoa butter-like fraction was approximately 36%, based on the weight of the starting materials.

Three pilot plant runs were made as described above. The yields and physical properties of the cocoa butter-like fractions obtained in the three runs were similar, indicating that the method of preparation was reliable and reproducible.

A fourth pilot plant run was made in which over 95% of the starting materials consisted of byproducts from the first three runs; that is, the starting materials consisted essentially of the hard fat which separated out of the acetone solution at room temperature and the low-melting fat which stayed in the acetone solution at 29° F. The cocoa butter-like fraction obtained in the fourth run was quite similar to the cocoa

butter-like fractions obtained in the first three runs, indicating that the process employed is such that the starting materials can eventually be converted almost completely into cocoa butter-like fat.

The cocoa butter-like fractions were combined to obtain a composite sample of about 140 pounds. The composite sample, hereafter referred to as Sample No. 1, had the following characteristics:

| | |
|---|---|
| Melting point............................. | 136° F. |
| Slip point............................. | ca. 118° F. |
| Iodine value........................... | ca. 27.3 |
| Free fatty acids, as oleic............. | ca. 0.2% |
| Trisaturated and other high-melting glycerides.............. | ca. 18% |

While the point of complete melting of the sample was relatively high, approximately 80% of the fat melted fairly sharply at the melting point of cocoa butter. The unexpectedly high content of trisaturated glycerides was responsible for the high melting point. However, the presence of the trisaturated glycerides was deemed to be not too objectionable.

Sample No. 1 was not completely bland in flavor and odor. One or two of the four pilot plant batches were practically free of flavor and odor, but the others contained a fair amount, which was introduced during the removal of the acetone during processing. It was found that mild deodorization produced a bland product and apparently did not affect the physical properties. However, Sample No. 1 was not deodorized because its flavor and odor were considered to be not too objectionable.

Portions of the 140-pound sample of cocoa butter-like fat were sent to eight individuals on the Research and Development Committee. Comments concerning the fat were received from several of these.

The solids content index of the fat was determined by at least two of the recipients. There was agreement that the fat, when compared with cocoa butter, containes less solids at low temperatures and more solids at high temperatures. In other words, the plastic range of the cocoa butter-like fat was considerably longer than that of cocoa butter. Generally this is considered undesirable, though one individual was of the opinion that there might be an advantage to a "relatively flat solids curve" if the cocoa butter-like fat is to be used in combinations with cocoa butter.

A 20-pound portion of Sample No. 1 sent out for evaluation was used by the recipient to prepare two coating mixtures. In one cocoa powder was used as a flavoring agent while chocolate liquor was used in the other.

It was stated that considerable difficulty was experienced in tempering these coatings. The coating containing cocoa powder as the flavoring material had very poor contraction and was difficult to demold. That containing chocolate liquor was somewhat better, probably because there was more cocoa butter to contract.

The eating qualities of both coatings were stated to be poor without the addition of emulsifiers. However, the addition of Spans and Tweens[1/] and sugar esters was said to make them quite palatable.

Samples of the coatings were sent to a confectioner for his evaluation, and he confirmed the findings mentioned above. In addition he mentioned that the flavor was not as pleasant and agreeable as that obtained with similar coatings made with coconut fat. This last-mentioned comment probably can be disregarded because the cocoa butter-like fat can be deodorized and made completely bland in flavor and odor.

In further investigations at the Southern Regional Research Laboratory, dilatometric curves were obtained for both Sample No. 1 and a commercial cocoa butter produced by the Hershey Chocolate Corporation[1]. Percentages of solids at various temperatures were calculated from these curves and are recorded in the first three columns of Table I.

Table I. Percentages of Liquid Components of Cocoa Butter and Cocoa Butter-Like Fats.

| Temperature, °F. | Liquid Content, % | | |
|---|---|---|---|
| | Cocoa butter | Sample No.1 | Sample No. 1 after modification[a] |
| 32 | 0.6 | 2.9 | 3.6 |
| 41 | 1.9 | 3.6 | 4.5 |
| 50 | 4.1 | 5.7 | 7.1 |
| 59 | 6.8 | 8.7 | 10.9 |
| 68 | 10.8 | 13.8 | 17.3 |
| 77 | 16.7 | 29.3 | 36.6 |
| 86 | 36.1 | 39.0 | 48.8 |
| 90.5 | -- | 49.5 | 61.9 |
| 93.4 | 100.0 | -- | -- |
| 95 | -- | 74.4 | 93.0 |
| 98.6 | -- | -- | 100.0 |
| 104 | -- | 88.2 | -- |
| 113 | -- | 92.3 | -- |
| 122 | -- | 93.4 | -- |
| 131 | -- | 96.8 | -- |
| 136.4 | -- | 100.0 | -- |

a/ Theoretical values on removing from Sample No. 1 the 20% of fat melting above 98.6° F.

It should be pointed out that the values in Table I are actual percentages, not solid content indices. Also, these data were obtained with well-tempered samples in which practically all of the solid components were in the highest melting form.

When these data are plotted as curves, it becomes evident that the main difference between cocoa butter and the cocoa butter-like fat was the presence in the latter of high-melting components, probably mostly trisaturated glycerides. According to dilatometric data which were obtained, exactly 20% of Sample No. 1 remained unmelted at 98.6° F.

It was believed that removal of these high-melting glycerides should improve the characteristics of Sample No. 1. The waxy feeling in the mouth when the product was eaten should be decreased, contraction on solidification should increase, and the tempering problems should be less severe.

To confirm the belief that Sample No. 1 could be improved by removal of the high-melting components, portions of it were warmed to 98.6° F., and those components which remained unmelted at this temperature were separated mechanically.

At temperatures below 98.6° F., modified Sample No. 1 contained the percentages of solids shown in Table I.

A five-pound portion of modified Sample No. 1 was sent to one of the members of the Research and Development Committee. This member made a confectionery coating with the fat and after some testing submitted the coating to another confectioner for further evaluation. Both individuals agreed that the removal of the higher melting components improved the fat.

Also, it was stated that the modified sample was appreciably easier to handle and melted down in the mouth considerably better. However, the coating made with the modified fat still was difficult to temper and still did not have enough contraction on solidification at the usual demolding temperatures. The coating which was made was said to be exceptionally brittle.

While modified Sample No. 1 was being evaluated, investigations were carried out to determine how the process of making the cocoa butter-like fat could be changed to obtain a better end product. Temperature vs. yield curves were obtained for the fractional crystallization step. The effect of holding time at the crystallization temperatures, the effect of small amounts of water in the acetone, and the effect of changing the solvent to fat ratio were investigated. At some ratios two liquid phases and one solid phase were found instead of the desired liquid and solid phase. On a laboratory scale, products were obtained over several temperature intervals and these products were evaluated. Methods of reducing the liquid content of the cocoa butter-like fat, and thereby increasing the ease of demolding, were considered.

On the basis of information obtained in all of the above described work, a new cocoa butter-like fat, Sample No. 2, was prepared. In the new preparation, 75 pounds of completely hydrogenated cottonseed oil and 25 pounds of triolein product, both supplied by the E. F. Drew & Company[1/], were mixed and rearranged in the presence of the usual catalyst. Then the rearranged product was dissolved in anhydrous acetone, 4 parts of solvent to 1 part of fat, and the solution was slowly cooled. The cocoa butter-like

fraction which was collected was that portion of the reaction product which precipitated out of solution between 68 and 32° F. After evaporation of most of the adhering acetone, the cocoa butter-like fraction was melted and an inert gas was passed through the liquid fat to remove the last trace of acetone.

Preliminary examination of this latest cocoa butter-like fat, Sample No. 2, showed that it had an iodine value of 26.3 and that practically all of it apparently melted over the temperature interval 91 - 97° F. More extensive tests are being made.

An approximately 10-pound portion of Sample No. 2 was given a mild deodorization at about 200° F. and then sent to a member of the Research and Development Committee for evaluation in coating compositions.

While the problem of making a good cocoa butter-like fat from domestic oils cannot yet be considered as being solved, definite progress is being made. It still is anticipated that a process similar to that which has been described can eventually be made to produce a good cocoa butter-like fat at an economically feasible cost.

B. <u>Properties of the Components of Confectionery Fats</u>

<u>Objective</u>. Cocoa butter and other confectionery fats are not single compounds. Each fat is actually a mixture. Even cocoa butter, which contains the least number of compounds, contains over six.

Unfortunately, not much information is available on the physical properties of the individual components of confectionery fats. Yet, to obtain the best performance from such fats, to select the best fats for particular uses, to blend fats properly, and to develop new and improved

fats, such information is needed. In order to develop this information, some of the major components of confectionery fats have been synthesized to obtain them in a pure form, and their properties are being determined.

Major Components of Cocoa Butter. The two compounds 2-oleopalmitostearin and 2-oleodistearin comprise about 57% and 22% respectively, of cocoa fat. As mentioned in previous reports, these two compounds were synthesized and a determination of their physical properties was undertaken. Since the last report, an additional melting point has been found for each compound. The total number of solid forms in which each compound can exist is now at least four. The new melting points, together with those listed previously in Report No. 3, are given in Table II.

Table II. Melting Points of the Different Forms of 2-Oleopalmitostearin and 2-Oleodistearin

| Form | Melting Point, °F. | |
|---|---|---|
| | 2-Oleopalmitostearin | 2-Oleodistearin |
| I | 99.3 | 109.0 |
| II | 91.4 | 99.9 |
| III | 76.1 | 86.0 |
| IV | 64.8 | 73.0 |

The melting point of the lowest melting form of 2-oleopalmitostearin was found only under somewhat unusual conditions. Not only was it necessary for the melt to be chilled quickly, but the time at the chilling temperature had to be of short duration. When a minute sample was heated thoroughly to above 140° F., chilled for two seconds at 32° F., and then heated to 64.8° F., the sample melted and remained

melted for one or two seconds. Holding the quick-chilled sample at 32° F. for short periods of time over two seconds and then heating it to 64.8° F. produced a pronounced change in translucency, but the sample did not melt completely. As the tempering time at 32° F. increased beyond about 40 seconds, the change in translucency became more difficult to detect.

The melting behavior of 2-oleodistearin was similar to that of 2-oleopalmitostearin insofar as the instability of the lowest melting solid form was concerned.

The transformation of the solid forms of the two compounds was found to be irreversible; that is, the transformation was always from a lower melting form to a higher melting form. For each compound the stability of the different forms increased as their melting points increased. In each case several days of tempering just below the melting point of the next-to-highest melting form was necessary to convert it into the highest melting form.

The rates of transformation were found to be most rapid when single, pure compounds were tested. In mixtures with each other and with other fats the rates at which 2-oleopalmitostearin and 2-oleodistearin could be tempered decreased greatly. More information on the ease of tempering in various mixtures will be obtained.

The rates of volumetric expansion were calculated from dilatometric curves for three solid forms and the liquid form of each of the two compounds. Melting dilations were calculated whenever this was possible. These data, together with comparative data for cocoa butter, are recorded in Table III.

Table III. Expansivity and Melting Dilation of 2-Oleopalmitostearin, 2-Oleodistearin, and Cocoa Butter

| Product | Form | Expansivity,a/ %/°F. | Melting Dilation,b/ % |
|---|---|---|---|
| 2-Oleopalmitostearin | I | 0.015 | 12.4 |
| | II | 0.024 | 10.0 |
| | III | 0.028 | 7.3 |
| | Liquid | 0.043 | --- |
| 2-Oleodistearin | I | 0.010 | 11.2 |
| | II | 0.026 | 9.1 |
| | III | 0.029 | --- |
| | Liquid | 0.043 | --- |
| Cocoa Butter | I | 0.025 | 9.5 |
| | II | 0.035 | 6.3 |
| | Liquid | 0.043 | --- |

a/ Solid forms measured at 32° F., liquid form at 122° F.

b/ Calculated at dilatometric melting point.

Dilatometric data also were obtained for mixtures of 2-oleopalmitostearin and 2-oleodistearin. In each case the mixture behaved like a single compound.

A manuscript describing in detail this investigation and the results obtained has been submitted to and accepted by the Journal of the American Oil Chemists' Society and should be published in the near future.

<u>2-Palmito-oleostearin</u>. In preparing a cocoa butter-like fat by the process described above a good proportion of the fat will consist of compounds which will be identical with the major components of cocoa butter insofar as the building blocks of the compounds are concerned but will differ in spatial arrangements. The chemist refers to these compounds as positional isomers. Thus 2-palmito-oleostearin is a positional isomer of 2-oleopalmitostearin, the major component of cocoa butter. 2-Palmito-oleostearin is one of the important compounds in a cocoa butter-like fat prepared as described above.

A pure sample of 2-palmito-oleostearin has been synthesized in the laboratory. The physical properties of this compound alone and in mixtures with the components of cocoa butter will be determined. As one phase of the planned investigation it will be determined under what conditions and to what extent solid solutions and eutectics are formed. Special equipment for carrying out these determinations has been devised and set up in the laboratory, and preliminary determinations are now underway. It is anticipated that when these and related tests have been completed, necessary information as to the compositional requirements of cocoa butter-like fats will have been obtained.

## C. <u>Moisture Transmission Through Fats</u>

The results of the first phase of this investigation were summarized rather fully in Report No. 3. Since that time additional confirmatory data have been obtained, and a manuscript entitled "Permeability of Some Fat Products to Moisture" has been prepared and submitted to the Journal of the American Oil Chemists' Society for

publication. Also a paper entitled "Moisture Transmission Through Fats" was presented at the Thirteenth Annual Production Conference of the Pennsylvania Manufacturing Confectioners' Association, Lancaster, Pennsylvania, April 22-24, 1959. Copies of this address can be obtained on request.

Additional research work on the transmission of moisture through fats is currently underway. The effects of a number of factors in moisture transmission remain to be investigated.

D. Effect of Composition and Polymorphic Form on Hardness

The development of an instrument and technique for measuring precisely the hardness of confectionery fats was described in Report No. 3, and it was indicated that the method should be useful in characterizing fats. During the past year additional data on the effect of composition and polymorphic form on the hardness of fats was obtained.

It was found that when normally solid fats are melted and quickly solidified and then stored at room temperature, their hardness may increase over a period of months. Cocoa butter which has been melted and quickly solidified will behave in a similar manner. Moderate increases in the temperature of storage generally increased the rate of hardening. However, when the storage temperature was increased too much, the hardness, measured at room temperature, actually decreased. This decrease was presumed to be caused by the formation of relatively large, soft crystals.

The addition of liquid oils to solid fats greatly decreased the hardness of the latter, the larger the amount added the greater was the decrease. Fats containing a sizable proportion of liquid component tended to decrease in hardness on storage at room temperature.

A manuscript entitled "Effect of Composition and Polymorphic Form on the Hardness of Fats" has been prepared and submitted for publication in the Journal of the American Oil Chemists' Society.

E. Slab Oils

Representatives of the National Confectioners' Association have in the past expressed an interest in testing edible and digestible oils which might be used as slab oils in the manufacture of candies. One fat product which should have some of the desired characteristics was prepared. The product consisted essentially of a mixture of dibutyrostearin and dibutyropalmitins, true fats whose building blocks (glycerol and butyric, palmitic, and stearic acids) occur in milk fats. This mixture of fats is completely saturated, and in the presence of a minute amount of antioxidant is highly resistant to rancidity. The mixture is liquid at room temperature and resembles ordinary vegetable oils. One disadvantage is that any degradation or abuse of the product may produce a butter-like flavor and odor.

Three batches of the product have been prepared and at one time or another sent to a few members of the Committee. The first two products possessed a mild flavor and apparently were found to be undesirable on that basis. The last batch was quite bland. Reports of the performance of the last batch have not yet been received.

FUTURE WORK

Major emphasis will be placed on the development of a satisfactory cocoa butter-like fat using domestic oils or their derivatives as

starting materials. Additional samples of cocoa butter-like fat will be prepared in the pilot plant. A number of new tests relating to the performance and characteristics of the several samples of cocoa butter-like fats will be made.

Additional work on the permeability of confectionery fats to water vapor will be undertaken. Several factors affecting permeability remain to be investigated. For example, the effect of crystal size needs to be established.

Because of its close relationship to the development of cocoa butter-like fats, the determination of the physical properties of confectionery fats and their components will be continued. One phase will be concerned with determining the compatability of 2-palmito-oleostearin, a major component of the cocoa butter-like fats, with 2-oleopalmitostearin and 2-oleodistearin, the major components of cocoa butter.

Several additional problems relating to the use of confectionery fats could be undertaken if more effort could be applied to the research. Among these is the development of techniques for speeding the tempering of fat products. Possibly this could be accomplished by the use of proper crystal nuclei.

The development of new-type fats to meet special needs should be given consideration and undertaken. The new-type fats should include improved slab oils, gloss oils, and waxes, and fats having unusual melting characteristics to serve special and specific purposes.

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